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A One-Step Method for the Synthesis of a Vinyl-Containing Silsesquioxane and Other Organolithic Macromolecular Precursors

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Introduction

Octasilsesquioxanes are well-known molecules that are presently being used as molecular building blocks in the synthesis of ceramic materials.[1] These materials are synthesized by a variety of means, including mixing several different solution species,[1d] photochlorination of $[Si_8O_{12}]H_8$ followed by treatment with neat methyl cyanide,[1a] use of acetic acid and trimethoxysilane saturated with anhydrous HCl,[2] and employment of excess reactants and long time scales (1−3 years).[3] These methods were inconvenient because they were multistep procedures that used high quantities of starting materials and long reaction times, and delivered low yields of the desired products. Recently, Moran *et al.*[4] reported a simple method for the synthesis of octakis(dimethylsiloxyl)octasilsesquioxane, $[Si_8O_{12}](OSi(CH_3)_2H)_8$. Their method involves the treatment of tetramethylammonium silicate with chlorodimethylsilane in a mixed organic solvent.[4] A one-step synthesis for the introduction of a vinyl functional group onto an octasilsesquioxane molecule has now been developed using the method of Moran. The target molecule, octakis(vinyldimethylsiloxyl)octasilsesquioxane, $[Si_8O_{12}](OSi(CH_3)_2(CHCH_2))_8$, is synthesized in high yields using tetramethylammonium silicate and chlorodimethylvinylsilane. The target molecule and several new derivatives have been synthesized and characterized by high-resolution ^{1}H, ^{13}C, and ^{29}Si NMR and by IR. This method is more practical than previous synthesis schemes for the preparation of the vinyl derivative.[1] This new synthesis route allows for the rapid formation of an air-stable silsesquioxane molecule that is easily derivatized to form new organolithic macromolecular materials (OMM's).

Experimental Section

Tetramethylammonium hydroxide (10% aqueous solution), silicic acid, and anhydrous HBr were used as purchased from Aldrich Chemical Co. Chlorodimethylvinylsilane (Aldrich) was distilled in an inert atmosphere immediately before use. Diethyl bromomalonate (Aldrich) was distilled prior to use.

Infrared spectra were recorded on a Nicolet 510P FTIR spectrometer using a resolution of 2 cm^{-1} in KBr. NMR spectra were recorded on a General Electric Omega (^{1}H, 300 MHz; ^{13}C, 75.47 MHz; ^{29}Si, 59.70 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) with reference to internal tetramethylsilane. A detailed NMR analysis will be reported later.

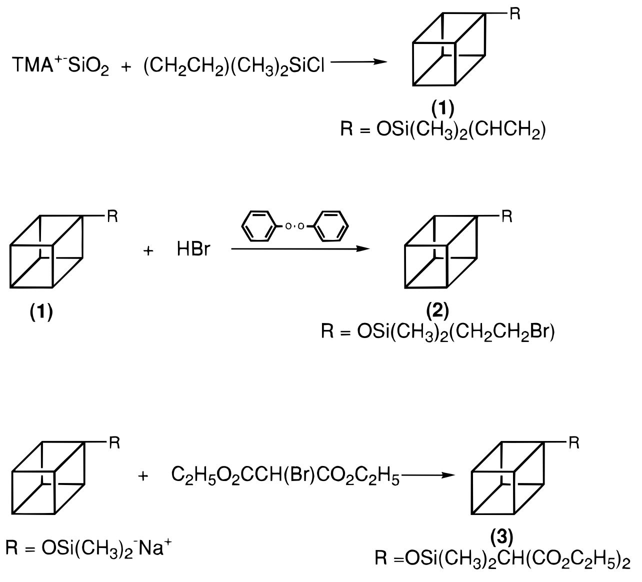

Figure 1. Synthetic scheme for octasilsesquioxane molecules. The square represents the core structure of $[Si_8O_{20}]$. There are eight R groups for each molecule, one occupying each corner of the cube.

Elemental analysis was performed by the Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory.

Synthesis of Octakis(vinyldimethylsiloxyl)octasilsesquioxane (1). The preparation of tetramethylammonium silicate has been detailed elsewhere.[4] Tetramethylammonium silicate (4.7 g) was added to a previously stirred solution of 124 mL of chlorodimethylvinylsilane, 100 mL of hexane, and 200 mL of dimethylformamide. This mixture was allowed to stir for 1 h and was then cooled in an ice bath at 0 °C for 30 min, after which it was hydrolyzed with 1 L of cold distilled water (added dropwise) to complete the formation of the siloxane. The mixture was removed from the ice bath and allowed to stir until room temperature was attained. The organic layer was separated from the mixture and washed with water until acid free. The organic layer was concentrated and placed in a freezer to complete crystallization of the product. The product was collected on a Buchner funnel (87% yield) and recrystallized from acetone/ethanol.[5] The final product was isolated as a white solid.[6]

Synthesis of Octakis((bromoethyl)dimethylsiloxyl)octasilsesquioxane (2). To a solution of **1** in hexane was added 0.0015 mol of benzoyl peroxide, and the mixture was stirred until the peroxide was completely dissolved. The solution was then saturated with anhydrous hydrogen bromide for 30 min using a fritted gas dispersion tube. The hydrogen bromide gas flow was removed, and the solution was allowed to stir at room temperature for 1 h. The mixture was then sparged with dry nitrogen to remove excess hydrogen bromide and concentrated to dryness. The resulting anti-Markovnikov addition product was isolated as a waxy solid. The final product was recrystallized from acetone/ethanol[7] (yield 79%).

Synthesis of Octakis((diethylmalonyl)dimethylsiloxyl)octasilsesquioxane (3). A solution of octakis(dimethylsiloxyl)octasilsesquioxane[4] in hexane was allowed to react with a solution of rigorously anhydrous

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[5] Structure and purity were established by comparison of mass spectra and ^{1}H, $^{13}C\{^{1}H\}$, and $^{29}Si\{^{1}H\}$ spectra with those of the same compounds.[1,4]

[6] Anal. Calcd for $Si_{16}O_{20}C_{32}H_{72}$: C, 31.3; H, 5.87. Found: C, 30.5; H, 5.76. ^{1}H NMR ($CDCl_3$): δ 0.208 (s, CH_3), 5.959 (m, CH), 1.63 (d, CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 0.219 (Si−CH_3), 132.7 (Si−CH), 138.2 (CH_2). $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 0.531 (Si−CH_3), −109.1 (Si core). IR (in KBr, cm^{-1}): 2963, 1597, 1254, 1008, 559.

[7] Anal. Calcd for $Si_{16}O_{20}C_{32}H_{80}Br_8$: C, 20.5; H, 4.27. Found: C, 20.9; H, 4.31. ^{1}H NMR ($CDCl_3$): δ 0.238 (s, CH_3), 1.484 (m, Si−CH_2), 3.596 (t, CH_2−Br). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 0.117 (Si−CH_3), 24.704 (Si−CH_2), 29.847 (CH_2−Br). $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 10.71 (Si−CH_3), −109.43 (Si core). IR (in KBr; cm^{-1}): 2902, 1785, 1450, 1225, 1072, 842, 557.

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methanol and sodium metal, previously combined to produce 8 mol equiv of sodium methoxide. This mixture was refluxed overnight to produce the sodium salt of octakis(dimethylsiloxyl)octasilsesquioxane. The sodium salt was concentrated to dryness and suspended in methanol, and the suspension was treated with 8.5 mol equiv of diethyl bromomalonate. The solution was allowed to reflux overnight in an inert atmosphere. The crude product (40% yield) was obtained by concentrating the reaction mixture to dryness. The purified product[8] was obtained by recrystallization from ethanol/water (27% yield).

Conclusion

The above reactions are easily scaled-up to provide large amounts of materials for further modifications. These will be reported later. This synthetic method for a vinyl-containing silsesquioxane provides a very simple, high-yield starting material used in the production of organolithic materials with varied properties. The bromine and malonate derivatives are new compounds which provide an alternative reactive site that can be easily modified to yield new silsesquioxane-based materials. These silsesquioxane-based derivatives are valuable compounds which can be used to form hybrid polymers of silicic acids[9] and new ceramic materials.[10] They may also find application in silicic polymer based sol−gel applications used for functional and corrosion protective coatings.[11]

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[8] Anal. Calcd for $Si_{16}O_{52}C_{72}H_{136}$: C, 37.9; H, 5.96. Found: C, 37.6; H, 6.01. ^{1}H NMR ($CDCl_3$): δ 0.210 ($Si-CH_3$), 4.87 (Si−CH), 4.30 (m, $O-CH_2$), 1.32 (t, CH_2-CH_3). IR (in KBr; cm^{-1}): 3463, 2959, 1748, 1640, 1438, 1260, 1097, 852, 806, 453.

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